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# Luminescence and energy transfer of single-phase white-emitting phosphor $\text{Ba}_2\text{Mg}(\text{PO}_4)_2:\text{Ce}^{3+}, \text{Eu}^{2+}$ for white LEDs†

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A series of  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2:\text{Ce}^{3+}, \text{Eu}^{2+}$  phosphors were synthesized by the traditional high temperature solid-state method, and the crystal structures and luminescence properties of the samples were discussed systematically. The energy transfer from  $\text{Ce}^{3+}$  to  $\text{Eu}^{2+}$  in  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2$  was proved to be of resonant type via a dipole–dipole interaction mechanism. With a precisely controlled relative proportion of  $\text{Ce}^{3+}/\text{Eu}^{2+}$ , the emission color of the samples can vary from blue (0.157, 0.071) to white (0.352, 0.332) and ultimately to yellow (0.452, 0.466) under the 323 nm ultraviolet light radiation excitation. The result reveals that the  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2:\text{Ce}^{3+}, \text{Eu}^{2+}$  phosphor may have potential application as a single-phased white-emitting phosphor for light emitting diodes.

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## 1. Introduction

In recent years, white light emitting diodes (LEDs) have attracted the attention of domestic and foreign researchers due to their energy saving, high efficiency, long life, and other advantages.<sup>1</sup> At present, white LEDs can be achieved by combining a blue InGaN LED chip with a yellow phosphor, YAG:Ce, which shows a poor color rendering index ( $R_a \approx 70\text{--}80$ ) and high CCT (CCT  $\approx 7750$  K) due to a lack of red component.<sup>1</sup> To solve these problems, white LEDs can also be fabricated by near-ultraviolet (UV) LED or UV-LED pumping red/green/blue multi-phased phosphors or a single-phase white emitting phosphor.<sup>2–4</sup> Generally, a white emitting phosphor can be obtained by controlling the concentration of several rare earths, however, due to the lack of certain light components, the obtained white phosphor shows a low color rendering index and cannot be applied in practice.<sup>6–11</sup> Therefore, the discovery of new phosphors, the design of crystal structure and the optimization of luminescence performance are still the hot spots of current research. Actually, the method of obtaining white light phosphor by using two kinds of rare earth ions doped together to generate energy transfer is the most popular among researchers. The phosphor obtained by this method presents a wide spectrum coverage. In addition, since there are only two types of activated ions, there are fewer energy transfer processes

and relatively less energy loss. Therefore, this is an ideal method at present. In the process of obtaining single-phase white emitting phosphor, the choice of two kinds of activated particles is also crucial. Generally, the selected activated ions are two rare earth ions or rare earth/transition metal ions. Under the condition of energy level matching, energy transfer can occur between the doped activation ions, such as  $\text{Ce}^{3+}/\text{Eu}^{2+}$ ,  $\text{Ce}^{3+}/\text{Mn}^{2+}$  and  $\text{Eu}^{2+}/\text{Mn}^{2+}$ .<sup>2–6</sup> Considering that the luminescence properties of  $\text{Ce}^{3+}$  and  $\text{Eu}^{2+}$  ions are relatively good, and the spectral coverage is wide, especially for  $\text{Eu}^{2+}$  ions, their spectral coverage can be from ultraviolet to near infrared, hence the researchers are more inclined to use  $\text{Ce}^{3+}/\text{Eu}^{2+}$  co-doping to obtain white emission, this work also uses this method to obtain white emitting phosphor.<sup>7–26</sup>

To the best our knowledge, in addition to the selection of activated ions, the matrix materials is also very important. For the host materials of phosphors, phosphate compounds are widely used currently owing to the facile synthesis, environmental-friendly characteristics and high stabilities, such as  $(\text{Ca}, \text{Sr})_9\text{Sc}(\text{PO}_4)_7:\text{Eu}^{2+}, \text{Mn}^{2+}$ ,<sup>27</sup>  $\text{Ca}_{9-x-y}\text{Ce}(\text{PO}_4)_7:\text{xEu}^{2+}, \text{yMn}^{2+}$ <sup>28</sup> and  $\text{Ca}_9\text{La}(\text{PO}_4)_7:\text{Eu}^{2+}$ .<sup>29</sup>  $\text{BaMg}_2(\text{PO}_4)_2$  is an alkaline earth phosphate compound with a rigid tetrahedral three-dimensional structure. Its physical and chemical properties are stable. Although the luminescence performance of  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2:\text{Eu}^{2+}$  has been widely investigated,<sup>30–36</sup> however, a systematic study on the energy transfer between  $\text{Eu}^{2+}$  and  $\text{Ce}^{3+}$  in  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2$  was not reported. In this work, the crystal structure of  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2$  and preferred crystallographic sites for activators were reported. The structure of  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2$  is monoclinic with space group  $P2_1/n$  ( $Z = 4$ ). There are two  $\text{Ba}^{2+}$  sites in this crystal lattice, one is 7 coordination, the other is 8 coordination, which can be replaced by rare earth dopants. The luminescence properties of  $\text{Eu}^{2+}$  and  $\text{Ce}^{3+}$  in  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2$  is

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demonstrated. After co-doping with  $\text{Ce}^{3+}$  ions, the emission intensity of  $\text{Eu}^{2+}$  ions was enhanced and a novel blue-yellow tunable phosphor  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2:\text{Ce}^{3+}$ ,  $\text{Eu}^{2+}$  can be obtained by varying the relative ratio of  $\text{Ce}^{3+}/\text{Eu}^{2+}$  under the irradiation of 323 nm light. Moreover, the energy transfer process and mechanism between  $\text{Ce}^{3+}$  and  $\text{Eu}^{2+}$  has been discussed systematically.

## 2. Experimental section

### 2.1 Synthesis

A series of  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2:x\text{Ce}^{3+}$ ,  $y\text{Eu}^{2+}$  phosphors were prepared by a traditional high-temperature solid-state method. The raw materials are  $\text{BaCO}_3$  (99.99%),  $\text{MgO}$  (99.99%),  $\text{NH}_4\text{H}_2\text{PO}_4$  (99.99%),  $\text{CeO}_2$  (99.99%) and  $\text{Eu}_2\text{O}_3$  (99.99%), which thoroughly mix and grind in an agate mortar for 20 min. Then powder mixtures were pre-heated in furnace at 500 °C for 2 h, and subsequently sintered at 1100 °C for 5 h in CO reducing atmosphere to get the final samples. Finally, the furnace temperature was lowered to room temperature, and the phosphor was ground before subsequent characterization.

### 2.2 Material characterization

The structure of samples is identified by powder X-ray diffraction (Bruker D8 X-ray diffractometer), with Ni-filtered  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15405$  nm), operating at 40 mA and 40 kV and recorded the patterns in the range of  $2\theta$  from 10° to 80°. The structural refinements were analyzed by General Structural Analysis System (GSAS) program. The steady time photoluminescence spectra including excitation (PLE) and emission (PL) spectra are measured in the range of 240 nm to 800 nm with scanning speed 1200 nm  $\text{min}^{-1}$  by a HITACHI F-4600 fluorescence spectrometer. The temperature dependent luminescence properties were measured on the same spectrophotometer, which was assembled with a TAP-02 high temperature fluorescence controller. The decay curves of the photoluminescence are acquired by FLS920 fluorescence spectrometer.

## 3. Results and discussion

### 3.1 Phase formation and structure of $\text{Ba}_2\text{Mg}(\text{PO}_4)_2$

It was reported that  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2$  (BMPO) is member of apatite-type family, which has a monoclinic structure with space group  $P_12_1/n_1$ .<sup>37</sup> The crystal structure of BMPO is shown in Fig. 1a. There are two types of Ba ions polyhedrons in this host, and Ba ions polyhedrons are accommodated in the tunnels that come out of three-dimensional framework of  $\text{MgO}_6$  and  $\text{PO}_4$  tetrahedrons. The  $\text{Ba}_1$  is surrounded by eight O atoms and  $\text{Ba}_2$  coordinate with seven O atoms. The Rietveld refinement with the results of BMPO presented in Fig. 2b, and the Rietveld refinement method has been conducted with GSAS. More XRD patterns and refined parameters are in Fig. S1 and Table S1,<sup>†</sup> and the diffraction peaks of the samples are well matched with the standard card BMPO (ICSD#59253), and no other impurity peaks are found, indicating the samples are all single crystal pure phase samples.

### 3.2 Luminescence properties of $\text{Ba}_2\text{Mg}(\text{PO}_4)_2:\text{Ce}^{3+}$

Fig. 2a and b show the emission spectra and excitation spectra of  $\text{BMPO}:x\text{Ce}^{3+}$  ( $x = 0.003\text{--}0.07$ ). It can be seen that under the excitation of 323 nm, the emission spectra of  $\text{BMPO}:x\text{Ce}^{3+}$  show an asymmetric emission band with a peak around 407 nm, which originates from the transition from 5d to 4f ground state. The excitation spectrum recorded by monitoring the emission of 407 nm consists of a stronger excitation band centered at 323 nm, and the spectrum goes from 220 nm to 380 nm. The insets of Fig. 2a and b present the emission intensity of  $\text{Ce}^{3+}$  ions with its concentration, respectively. The intensities both increase with its concentration. The intensity reaches the strongest at  $x = 0.05$ , and then the intensity gradually decreases due to the quenching effect of the activated ions. It is well known that  $\text{Ce}^{3+}$  emission should be composed of a double band due to the splitting of its 4f ground state, and the energy difference of this splitting between  $^2\text{F}_{7/2}$  and  $^2\text{F}_{5/2}$  of  $\text{Ce}^{3+}$  is about 2000  $\text{cm}^{-1}$ . In this study, the asymmetric emission band can be decomposed into two well-separated Gaussian

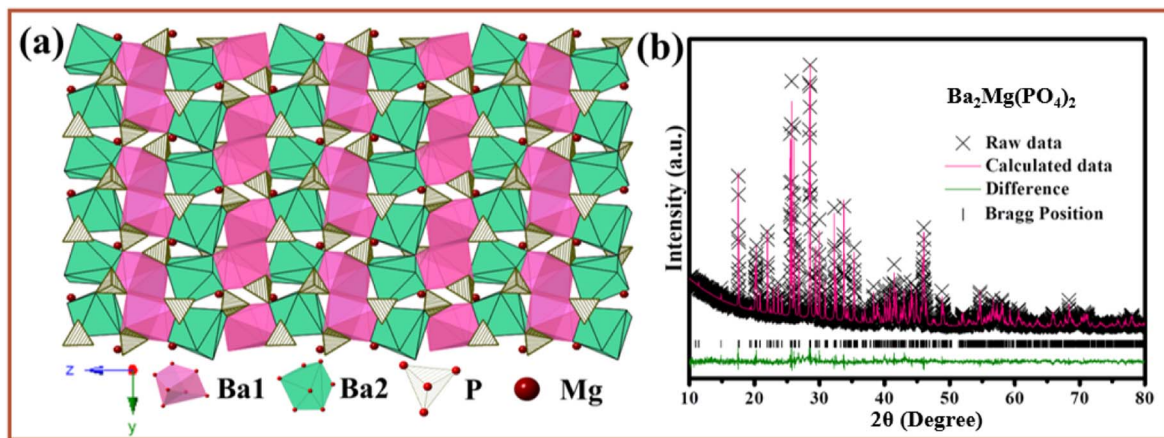


Fig. 1 (a) Crystal structure of  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2$ . (b) Powder XRD patterns for Rietveld structure analysis of  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2$  based on the  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2$  ICSD#59253 phase model.

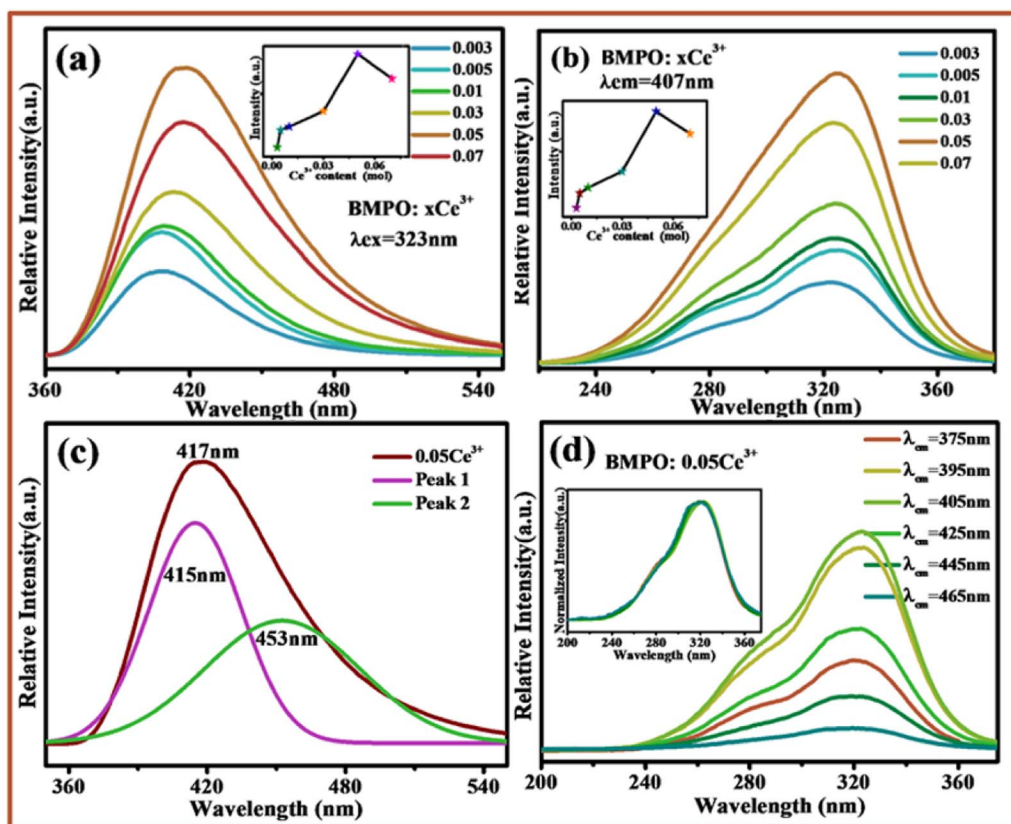


Fig. 2 (a) Excitation spectra of  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2:\text{xCe}^{3+}$  ( $\lambda_{\text{em}} = 407 \text{ nm}$ ). (b) Emission spectra of  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2:\text{xCe}^{3+}$  ( $\lambda_{\text{ex}} = 323 \text{ nm}$ ). (c) Emission spectra and the two sub-peaks of  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2:0.05\text{Ce}^{3+}$  ( $\lambda_{\text{ex}} = 323 \text{ nm}$ ). (d) Excitation spectra of  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2:0.05\text{Ce}^{3+}$  for the different emission wavelengths, the insert describes the normalized excitation spectra.

components with maxima at 415 nm and 453 nm, as shown in Fig. 2c, and the energy difference between the two sub peaks is about  $2021 \text{ cm}^{-1}$ , which is close to the theoretical energy difference between the  $^2\text{F}_{7/2}$  and  $^2\text{F}_{5/2}$  levels. In order to further determine the source of the two sub peaks, the excitation spectra of the sample  $\text{BMPO}:0.05\text{Ce}^{3+}$  at 375 nm, 395 nm, 405 nm, 425 nm, 445 nm and 465 nm were monitored, as shown in Fig. 2d. The inset shows the normalized excitation spectrum. It can be seen from the figure that, except for the difference in luminous intensity, the spectral types of all excitation spectra are completely the same, which indicates that the  $\text{Ce}^{3+}$  ion is very likely to have only one luminescence center. This proves the asymmetry emission peak of  $\text{BMPO}:0.05\text{Ce}^{3+}$  is caused by the spin-orbit coupling effect of  $\text{Ce}^{3+}$ .

### 3.3 Luminescence properties of $\text{Ba}_2\text{Mg}(\text{PO}_4)_2:\text{Eu}^{2+}$

Fig. 3a shows the excitation and emission spectra of  $\text{BMPO}:0.07\text{Eu}^{2+}$ . Upon excitation at 350 nm,  $\text{BMPO}:0.07\text{Eu}^{2+}$  exhibits a broad emission band extending from 450 nm to 750 nm, and the emission peak is located at about 580 nm due to the  $4\text{f}^0 5\text{d}^1 \rightarrow 4\text{f}^1$  transition of  $\text{Eu}^{2+}$  ion. Monitored at 580 nm, the excitation spectra give a band with peak center at about 340 nm in the wavelength range of 250–450 nm. Fig. 3b shows the emission spectra of  $\text{BMPO}:\text{yEu}^{2+}$  with different  $\text{Eu}^{2+}$  concentration. It can be seen that the emission spectra consist

of a relatively symmetric broad band center at 580 nm. In order to clarify the influence of  $\text{Eu}^{2+}$  concentration on its luminescence performance, the normalized emission spectra of  $\text{BMPO}:\text{yEu}^{2+}$  are shown in Fig. 3c, when changed the concentrations of  $\text{Eu}^{2+}$  ions, the emission spectrum has not changed significantly, and there is no obvious red-blue shift. The emission intensities of  $\text{BMPO}:\text{Eu}^{2+}$  with different  $\text{Eu}^{2+}$  concentrations are shown in Fig. 3d. The emission intensities firstly increase with increasing the content of  $\text{Eu}^{2+}$ , the emission intensity is maximized at  $x = 0.07$ , and then decrease due to the concentration quenching effect.

For  $\text{BMPO}$ , there are three cation sites, namely  $\text{Ba}_1$ ,  $\text{Ba}_2$  and  $\text{Mg}_3$ . Among them,  $\text{Ba}_1$  is surrounded by eight O atoms,  $\text{Ba}_2$  is surrounded by seven O atoms, and  $\text{Mg}_3$  is surrounded by six oxygen atoms. Taking into account the degree of suitability of the doped ion and the substitute ion in radius and valence, there are only two lattice sites suitable for  $\text{Eu}^{2+}$  ions to enter, namely  $\text{Ba}_1$  and  $\text{Ba}_2$  sites. It can be found that the emission spectrum of  $\text{Eu}^{2+}$  ions is basically symmetrical, which indicates that  $\text{Eu}^{2+}$  ions are likely to occupy only one of the lattice sites and have only one luminescence center, which results in a relatively symmetrical emission spectrum. In order to clarify the number of luminescence centers,  $\text{BMPO}:0.07\text{Eu}^{2+}$  was subjected to a low-temperature spectrum test at 4 K and a fluorescence lifetime test at room temperature. Fig. 3e shows that the emission spectrum of  $\text{BMPO}:0.07\text{Eu}^{2+}$  has only one relatively



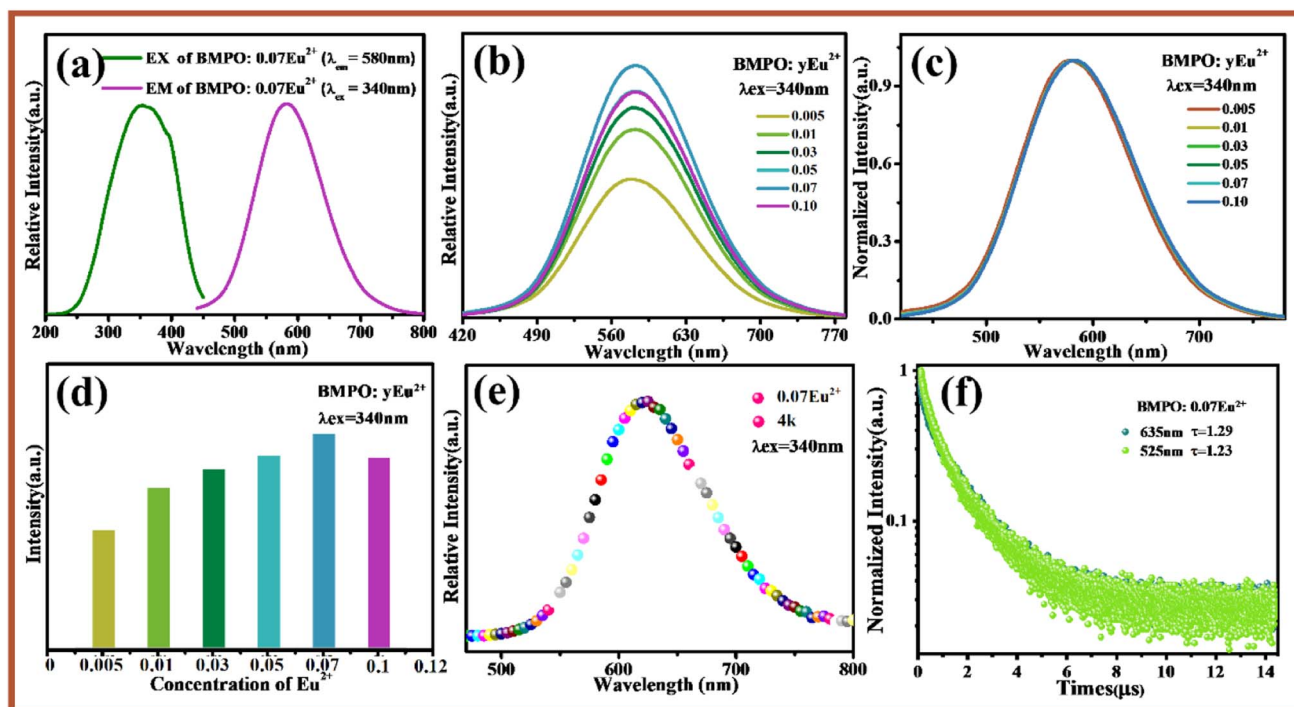


Fig. 3 (a) Excitation spectra and emission spectra of Ba<sub>2</sub>Mg(PO<sub>4</sub>)<sub>2</sub>:0.07Eu<sup>2+</sup>. (b) Emission spectra of Ba<sub>2</sub>Mg(PO<sub>4</sub>)<sub>2</sub>:yEu<sup>2+</sup> (λ<sub>ex</sub> = 340 nm). (c) The normalized emission spectra of Ba<sub>2</sub>Mg(PO<sub>4</sub>)<sub>2</sub>:yEu<sup>2+</sup>. (d) The emission intensity of Ba<sub>2</sub>Mg(PO<sub>4</sub>)<sub>2</sub>:yEu<sup>2+</sup> with the different concentrations of Eu<sup>2+</sup> ions. (e) The emission spectrum of Ba<sub>2</sub>Mg(PO<sub>4</sub>)<sub>2</sub>:0.07Eu<sup>2+</sup> at 4 K. (f) The lifetime decay curve at 525 nm and 635 nm emission peaks of Ba<sub>2</sub>Mg(PO<sub>4</sub>)<sub>2</sub>:0.07Eu<sup>2+</sup>.

symmetrical emission peak under the excitation of 340 nm, which proves that there is only one luminescence center. In order to further verify the number of luminescence centers, the decay curves of BMPO:0.07Eu<sup>2+</sup> monitored at 525 and 635 nm were tested and are presented in Fig. 3f, and the lifetimes of them are 1.23 and 1.29 μs. From the results, it can be seen that the lifetimes of the two emission peaks are almost the same, which further verifies that there is only one luminescence center of Eu<sup>2+</sup> ions in the BMPO.

Due to the special electronic configuration, Eu<sup>2+</sup> ion is particularly sensitive to the crystal field environment surrounding the central ion. In order to obtain the detailed structural information of BMPO:yEu<sup>2+</sup> and find out which lattice site Eu<sup>2+</sup> ions enter, the structure of BMPO:yEu<sup>2+</sup> (y = 0–0.1) by GSAS software based on the standard card of BMPO (ICSD#59253) were refined, and shown in Fig. S2 and Table S2.† It can be seen that all parameters meet the experimental requirements, which prove that the refinement results are true and reliable. The evolution of lattice parameters *a*, *b*, *c* and the unit cell volume *V* of BMPO:yEu<sup>2+</sup> (y = 0–0.1) is shown in Fig. S3.† It is found that parameters *a*, *b*, *c* and the unit cell volume decrease gradually with the increase of Eu<sup>2+</sup> content, which is caused by lattice shrinkage caused by Eu<sup>2+</sup> with smaller radius entering the lattice instead of Ba<sup>2+</sup> with larger radius. At the same time, it also shows that Eu<sup>2+</sup> ions are successfully doped in.

As shown in Fig. 4a, the refined crystal structure of BMPO:yEu<sup>2+</sup> (y = 0–0.1) was analyzed in detail and the volume changes of the lattice sites Ba<sub>1</sub> and Ba<sub>2</sub> were summarized.

According to the previous analysis, the radius of Eu<sup>2+</sup> is smaller than that of Ba<sup>2+</sup>. If Eu<sup>2+</sup> successfully occupies a certain lattice site after entering the host, it will definitely cause a change in the volume of this site is shown in Fig. 4b. It can be seen from the Fig. 4a that the volume of Ba<sub>1</sub> gradually decreases with the increase of Eu<sup>2+</sup> concentration, which is caused by the entry of Eu<sup>2+</sup> ions with a smaller radius into the site Ba<sub>1</sub>, while the volume of Ba<sub>2</sub> shows a slight increase first and then a slight decrease. Through analysis, it is found that the lattice sites Ba<sub>1</sub> and Ba<sub>2</sub> are connected to each other through the sides and apex angles. When Eu<sup>2+</sup> ions enter the Ba<sub>1</sub> lattice site, the unit cell volume of Ba<sub>1</sub> decreases, and the decrease of Ba<sub>1</sub> also has a pulling effect on Ba<sub>2</sub>, so that the volume of Ba<sub>2</sub> increases slightly. When the doping concentration of Eu<sup>2+</sup> ions is large, it cannot completely enter the Ba<sub>1</sub> site, and part of it will enter the gap in the lattice site, and the Eu<sup>2+</sup> ions that enter the gap will Ba<sub>1</sub> has a certain degree of squeezing effect, hence its unit cell volume is slightly reduced. In summary, Eu<sup>2+</sup> ions do occupy the Ba<sub>1</sub> site after entering the BMPO.

#### 3.4 Luminescence properties of BMPO:0.05Ce<sup>3+</sup>, yEu<sup>2+</sup>

Fig. 5a shows the emission spectra of BMPO:0.05Ce<sup>3+</sup>, yEu<sup>2+</sup> under excitation at 323 nm. Due to the 5d → 4f transition of Ce<sup>3+</sup> and Eu<sup>2+</sup>, there are two emission bands from 370 nm to 520 nm with a peak at 407 nm, and from 540 nm to 720 nm with a peak at 580 nm. With increasing the concentration of Eu<sup>2+</sup>, the emission intensity of Ce<sup>3+</sup> decreases monotonically. Meanwhile, the emission intensity of Eu<sup>2+</sup> increases gradually until the Eu<sup>2+</sup>



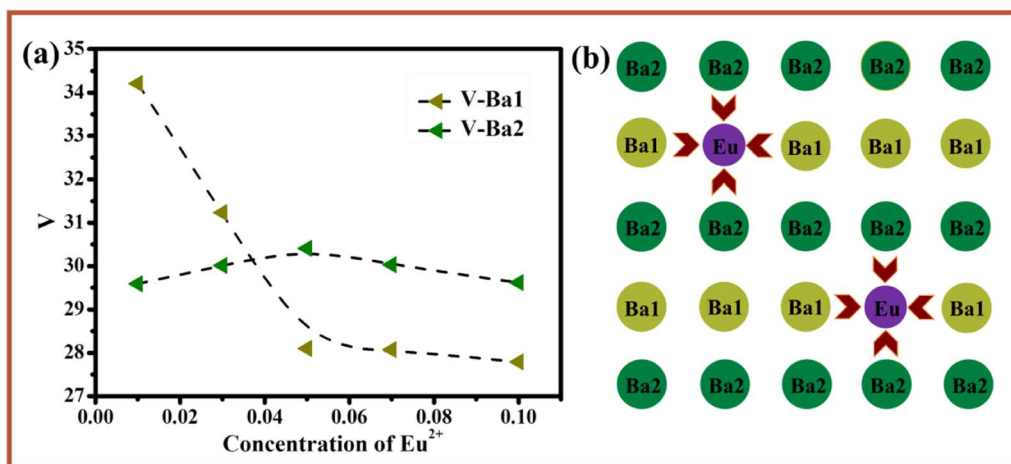


Fig. 4 (a) The lattice volume  $\text{Ba}_1$  and  $\text{Ba}_2$  with  $\text{Eu}^{2+}$  doping concentration in  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2:\gamma\text{Eu}^{2+}$ . (b) Schematic diagram of the lattice change after  $\text{Eu}^{2+}$  enters the host.

content is  $x = 0.07$  and the concentration quenching occurs is shown in Fig. 5b. In addition, the emission spectra of  $\text{Ce}^{3+}$  and excitation spectra of  $\text{Eu}^{2+}$  are also shown in Fig. 5c. A significant spectral overlap between the emission spectrum of  $\text{BMPO}:\text{0.05Ce}^{3+}$  and the excitation spectrum of  $\text{BMPO}:\text{0.07Eu}^{2+}$  is observed, which indicates that the energy transfer from the  $\text{Ce}^{3+}$  to  $\text{Eu}^{2+}$  ions can be expected in  $\text{BMPO}$ .

To further validate the energy transfer process between  $\text{Ce}^{3+}$  and  $\text{Eu}^{2+}$ , the decay curves of  $\text{Ce}^{3+}$  fluorescence lifetime for  $\text{BMPO}:\text{0.05Ce}^{3+}, \gamma\text{Eu}^{2+}$  were measured by monitoring at 407 nm with the excitation at 323 nm, and the measured decay curves are depicted in Fig. 6a. It is found that all the decay curves can be well fitted with a second-order exponential decay, which can be fitted using the eqn (1):<sup>38–40</sup>

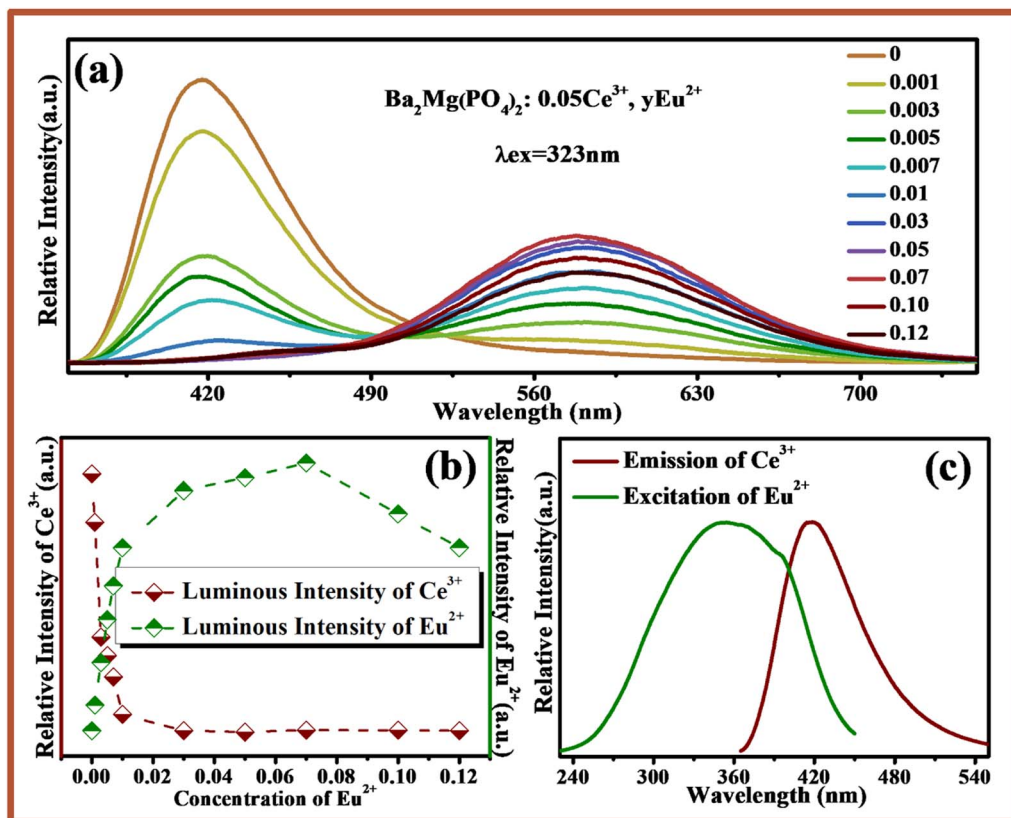


Fig. 5 (a) The emission spectra of  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2:\text{0.05Ce}^{3+}, \gamma\text{Eu}^{2+}$  ( $\lambda_{\text{ex}} = 323\text{ nm}$ ). (b) The luminous intensity of  $\text{Eu}^{2+}$  and  $\text{Ce}^{3+}$  varies with the concentration of  $\text{Eu}^{2+}$  ions. (c) The emission spectra of  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2:\text{0.05Ce}^{3+}$  and the excitation spectra of  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2:\text{0.07Eu}^{2+}$ .



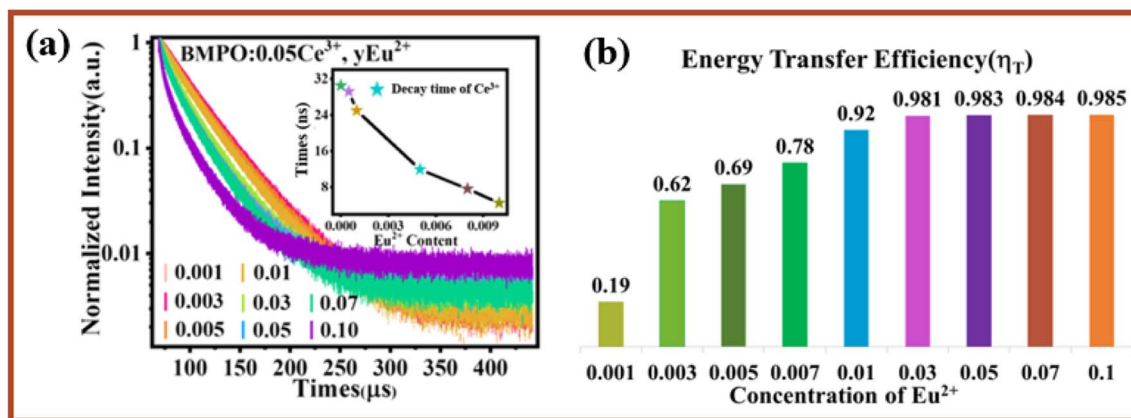


Fig. 6 (a) Decay curves of  $\text{Ce}^{3+}$  ions in  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2:0.05\text{Ce}^{3+}, y\text{Eu}^{2+}$  ( $\lambda_{\text{ex}} = 320 \text{ nm}$ ). (b) The energy transfer efficiency between  $\text{Ce}^{3+}-\text{Eu}^{2+}$  in  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2:0.05\text{Ce}^{3+}, y\text{Eu}^{2+}$ .

$$I(t) = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (1)$$

where  $I$  is luminescence intensity,  $A_1$  and  $A_2$  are constants,  $\tau$  is average lifetime, and  $\tau_1$  and  $\tau_2$  are lifetime for rapid and slow decays, respectively. The average lifetime  $\tau^*$  can be obtained using the formula (2):<sup>38–40</sup>

$$\tau^* = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2) \quad (2)$$

The effective decay time ( $\tau^*$ ) of  $\text{Ce}^{3+}$  ions were calculated to be 32.0170, 30.5329, 29.2241, 25.0169, 11.9310, 8.3924, 7.5280 and 4.4988 ns, respectively. Obviously, the lifetime values decreased monotonically as the  $\text{Eu}^{2+}$  concentration increased, which strongly demonstrates energy transfer from  $\text{Ce}^{3+}$  to  $\text{Eu}^{2+}$ . In addition, the energy transfer efficiency ( $\eta_T$ ) can be calculated using the following eqn (3).<sup>41–43</sup>

$$\eta_T = 1 - (I_s - I_{s0}) \quad (3)$$

where  $I_s$  and  $I_{s0}$  are luminescence intensity of sensitizer  $\text{Ce}^{3+}$  in the presence and absence of activator  $\text{Eu}^{2+}$ . As shown in Fig. 6b,

the energy-transfer efficiency increased sharply with the increasing of the  $\text{Eu}^{2+}$  content. The  $\eta_T$  value reached 98.5% at  $y = 0.1$ , which also indicated that the energy transfer efficiency of  $\text{Ce}^{3+}-\text{Eu}^{2+}$  can increase with increasing  $\text{Eu}^{2+}$  content.

Based on the above argument, there are the energy transfer from  $\text{Ce}^{3+}$  to  $\text{Eu}^{2+}$  ions, hence the determination of their energy transfer mechanism is also an important factor to study their energy transfer process. In general, the exchange interaction and multipolar interaction are the main types of interactions between sensitizer and activator.<sup>44</sup> With the increase of activator concentration, the distance between the sensitizer and the activator begins to approach, and there is an obvious energy transfer between the sensitizer and the activator. When the distance reaches the critical value, the energy transfer will be hindered. The critical distance  $R_{\text{Ce-Eu}}$  between  $\text{Ce}^{3+}$  and  $\text{Eu}^{2+}$  can be estimated by<sup>45,46</sup>

$$R_c = 2 \left[ \frac{3V}{4\pi X_c N} \right]^{\frac{1}{3}} \quad (4)$$

where  $V$  is the volume in the unit cell,  $N$  is the number of cations in the unit cell,  $X_c$  is the total concentration of  $\text{Ce}^{3+}$  ions and the

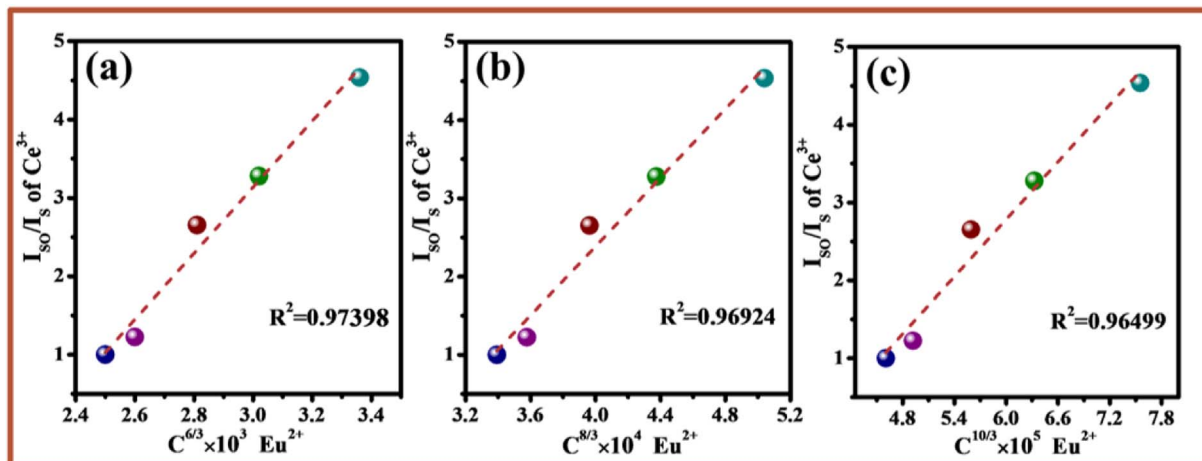


Fig. 7 Relationships between  $I_{s0}/I_s$  and  $C^{n/3}$ : (a)  $n = 6$ , (b)  $n = 8$ , (c)  $n = 10$ .



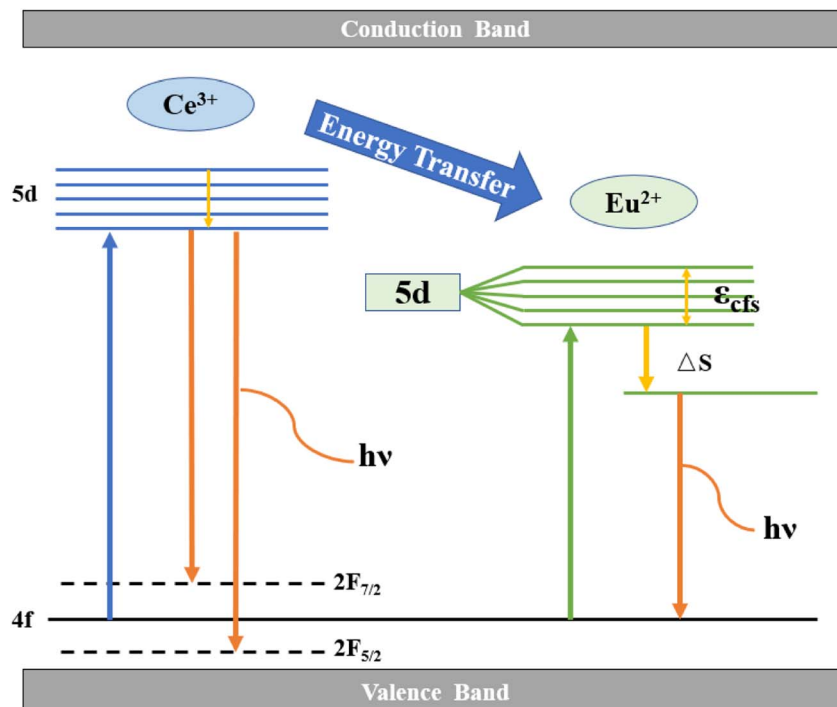


Fig. 8 Energy level scheme for ET in  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2:0.05\text{Ce}^{3+}, y\text{Eu}^{2+}$ .

critical concentration of  $\text{Eu}^{2+}$ . For BMPO host, the value of  $V$  is  $758.43 \text{ \AA}^3$  and  $N = Z = 4$ , the critical concentration of  $\text{Eu}^{2+}$  is 0.07. The critical distance of energy transfer is calculated to be about  $14.3 \text{ \AA}$  for  $\text{BMPO}:0.05\text{Ce}^{3+}, y\text{Eu}^{2+}$ , which is larger than the critical distance for exchange interaction ( $5 \text{ \AA}$ ). Therefore, the

interaction between  $\text{Ce}^{3+}$  and  $\text{Eu}^{2+}$  ions in BMPO might take place *via* multipolar interaction.

On the basis of Dexter's the formula of multipolar interaction and Reisfeld's approximation, the following relationship (5) can be obtained:<sup>47</sup>

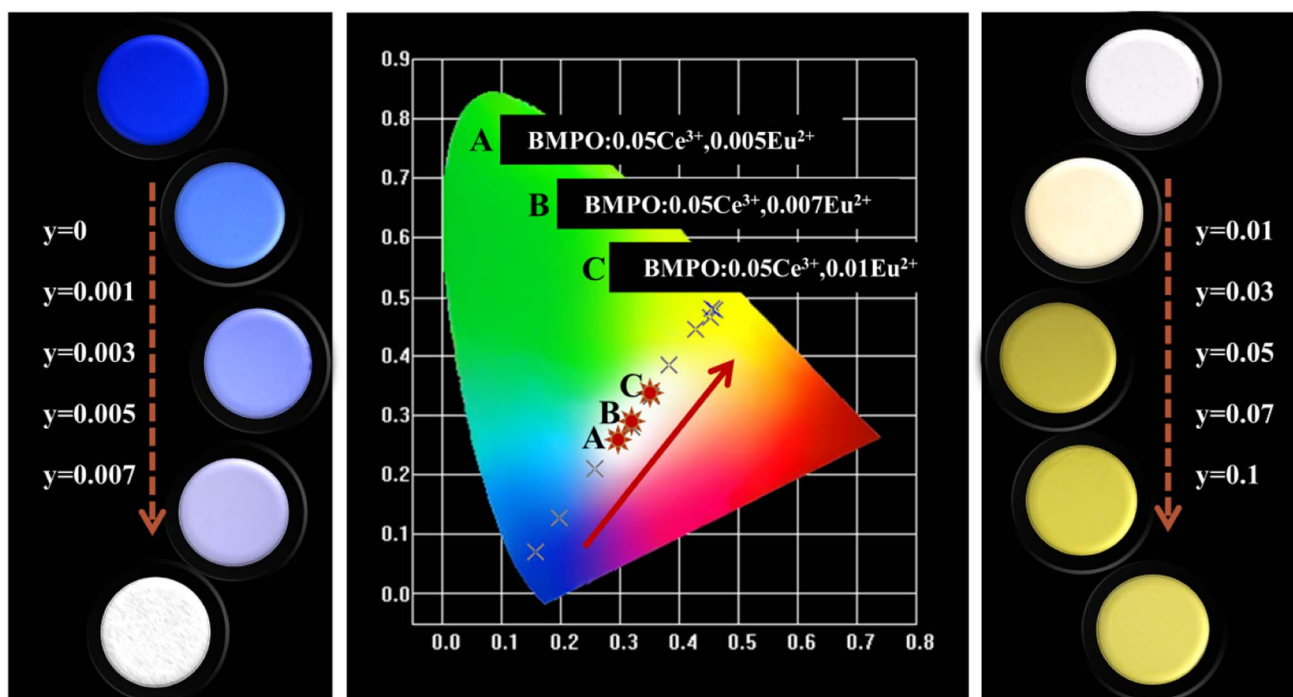


Fig. 9 The color coordinates and photographs of  $\text{Ba}_2\text{Mg}(\text{PO}_4)_2:0.05\text{Ce}^{3+}, y\text{Eu}^{2+}$  ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ).



$$\frac{I_{SO}}{I_S} \propto C_{\ln^{2+}}^{n/3} \quad (5)$$

where  $I_{SO}$  and  $I_S$  are the luminescence intensity of  $Ce^{3+}$  in the absence and presence of  $Eu^{2+}$ ,  $C$  is the total doping content of sensitizer ( $Ce^{3+}$ ) and activator ( $Eu^{2+}$ ), and  $n = 6, 8, 10$  corresponds to the dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively. The relationship of  $\frac{I_{SO}}{I_S} \propto C_{\ln^{2+}}^{n/3}$  is shown in Fig. 7a–c. Considering the fitting factor  $R^2$ , the relation  $\frac{I_{SO}}{I_S} \propto C_{\ln^{2+}}^{6/3}$  has the best fitting, implying that the energy transfer between  $Ce^{3+}$  and  $Eu^{2+}$  in BMPO occurs via a dipole–dipole interaction mechanism.

Fig. 8 describes the energy level transitions of  $Ce^{3+}$  and  $Eu^{2+}$  ions and the energy transfer mechanism of  $Ce^{3+}$ – $Eu^{2+}$  in BMPO. Under the 323 nm excitation, the electrons of  $Ce^{3+}$  ions transition from the 4f energy level to the 5d energy level. Because the exposed 5d orbital of  $Ce^{3+}$  is susceptible to splitting by the crystal field, and it has two ground states the electron configurations are  $2F_{7/2}$  and  $2F_{5/2}$ , respectively, hence they show a relatively wide emission range. At the same time, because the upper energy level of  $Eu^{2+}$  ions is lower than that of  $Ce^{3+}$  ions, they are excited to the 5d energy level. A part of the electrons will jump to the upper energy level of  $Eu^{2+}$  ion, and then return to the lower energy level and emit photon. Where  $\epsilon_{cfs}$  denotes the 5d energy level cleavage of  $Eu^{2+}$  and  $\Delta S$  is the Stokes shift, which is the energy transfer process of  $Ce^{3+}$ – $Eu^{2+}$ .

The chromaticity calculation was performed based on the luminescence spectra of BMPO:0.05 $Ce^{3+}$ ,  $yEu^{2+}$  under the 323 nm excitation, and the calculation results of the CIE coordinates and a series of digital photographs upon the 365 nm UV lamp are shown in Fig. 9. As the doping concentrations of  $Eu^{2+}$  ions are from 0 to 0.1, the color coordinates ( $x, y$ ) of BMPO:0.05 $Ce^{3+}$ ,  $yEu^{2+}$  shift from blue (0.157, 0.071) to yellow (0.452, 0.466). It is worth noting that the CIE chromaticity coordinates of BMPO:0.05 $Ce^{3+}$ , 0.005 $Eu^{2+}$ , BMPO:0.05 $Ce^{3+}$ , 0.007 $Eu^{2+}$  and BMPO:0.05 $Ce^{3+}$ , 0.01 $Eu^{2+}$  are (0.294, 0.257), (0.319, 0.279) and (0.352, 0.332), which are all located in the white light region. The results indicate that BMPO:0.05 $Ce^{3+}$ ,  $yEu^{2+}$  can be achieved by appropriately adjusting the ratio of Ce/Eu ions.

## 4. Conclusions

In summary, series color-tunable and single-composition white emitting phosphors BMPO:0.05 $Ce^{3+}$ ,  $yEu^{2+}$  were successfully synthesized. The samples could get varied color emission from blue (0.157, 0.071) towards white (0.352, 0.332) and ultimately to yellow (0.452, 0.466) under the excitation of 323 nm light by precisely controlling the relative proportion of  $Ce^{3+}/Eu^{2+}$ . The energy transfer from  $Ce^{3+}$  to  $Eu^{2+}$  in BMPO has been validated and the energy transfer mechanism is the dipole–dipole interaction. The results proved that the single-phased white emitting phosphor BMPO: $xCe^{3+}$ ,  $yEu^{2+}$  can be excited by UV-LED chips and has the potential application in white LEDs.

## Conflicts of interest

The authors declare no competing financial interest.

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